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Excess heat capacities of mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate, lactams and cyclic alkanones

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Abstract The molar heat capacities, C_P, of 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + pyrrolidin-2-one or 1-methylpyrrolidin-2-one (2) + cyclopentanone or cyclohexanone (3) ternary mixtures have been measured at 293.15, 298.15, 303.15 and 308.15 K and 0.1 MPa using micro-differential scanning calorimeter. The observed C_P data have been utilized to evaluate their excess heat capacities, $(C_P^E)_{123}$ values, and same have been fitted to Redlich–Kister equation to predict ternary adjustable parameters along with their standard deviations. The Moelywn-Huggins concept (Huggins in Polymer 12:389–399, 1971) of interactions between the surfaces of constituent molecules in binary mixtures has been extended to ternary mixtures using topology of the constituent molecules to obtain expression (Graph theory) that predict correctly the $(C_P^E)_{123}$ data of the present mixtures. The observed $(C_P^E)_{123}$ data have also been analyzed in terms of modified Flory's theory.

Keywords Density, ρ · 1-Ethyl-3-methylimidazolium tetrafluoroborate · 1-Methylpyrrolidin-2-one · Molar heat capacity, C_P · Excess heat capacity, C_P^E · Interaction energy parameter, χ

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Introduction

As challenge emerged in the burgeoning chemical industries and environmental pollution due to use of volatile organic solvents, researchers were confined in a box what they could and could not do. They explored ways to use new compounds like ionic liquids in place of traditional volatile and corrosive organic liquids to minimize their use. Creating new thermodynamic data on liquid mixtures containing ionic liquid due to their unique properties [1, 2] will foster new opportunities for their use in chemical industries. Heat capacity of liquid or liquid mixtures is one of the properties for use in thermal applications. Accurate heat capacity and excess heat capacity data of liquid/liquid mixtures are crucial (i) for the design and operation of heat transfer processes [3, 4] and (ii) for units such as fractionation tower used to separate mixture [5]. The sensitivity of tower's segment is determined by an energy balance which in turn involves liquid/liquid mixture enthalpy or heat capacity data. The use of ionic liquids due to their unique properties especially low volatility or their mixtures with organic liquids can be used as alternative sources in designing of equipments or environmental treatment technologies [6–9]. Ionic liquids having imidazolium cations are considered to be efficient ionic liquids for high absorption of carbon dioxide, diesel extractive desulfurization (EDS), oxidative desulfurization (ODS) and catalytic oxidative desulfurization (ECODS) and seem to be a good alternative for diesel desulfurization [10–14]. Further, several investigations on imidazolium-based ionic liquids possessing tetrafluoroborate anion have been carried out for their use in capacitors, solar cells, fuel cells and batteries [15–20]. Pyrrolidin-2-one and 1-methyl pyrrolidin-2-one have potential to be used in the solvent extraction process for separating polar substances from nonpolar substances,

petrochemicals and biological applications [21, 22]. Cyclopentanone and cyclohexanone are used as safety solvents and important intermediates for the synthesis of many organic compounds which are used in chemical, pharmaceutical and cosmetic industries [22–25]. Liquid mixtures consisting of 1-ethyl-3-methylimidazolium tetrafluoroborate, pyrrolidin-2-one, 1-methyl pyrrolidin-2-one, cyclopentanone and cyclohexanone may, therefore, comprise a class of mixtures of importance in chemical, pharmaceutical and biological industries. In continuation of our earlier studies on thermodynamic properties of binary/ternary liquid mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate as one of the component [26–29], we report here excess heat capacity, $(C_P^E)_{123}$, data of 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + pyrrolidin-2-one or 1-methyl pyrrolidin-2-one (2) + cyclopentanone or cyclohexanone (3) ternary mixtures.

Experimental

1-Ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4] (mass fraction: 0.980) was used without further purification. The water content in ionic liquid was regularly checked using Karl Fischer titration [30] and found to be less than 320 ppm. Pyrrolidin-2-one (2-Py) (mass fraction: 0.994) was purified by vacuum distillation over calcium oxide [31], 1-methyl pyrrolidin-2-one (NMP) (mass fraction: 0.992) was purified by fractional distillation under reduced pressure [32], and cyclopentanone (Fluka, mass fraction: 0.991) and cyclohexanone (Fluka, mass fraction 0.988) were purified by fractional distillation [33]. The source of liquids, along with methods of purification and final purity, is reported in Table 1. Densities, ρ, speeds of sound, u, and heat capacities, C_P, of the pure liquids at studied temperatures are listed in Table 2 and also compared with literature values [23, 25, 33–53]. The ρ and u values of the purified liquids were measured using a density and sound analyzer apparatus (Anton Paar DSA 5000) in the manner as described elsewhere [54, 55]. The uncertainties in the density and speed of sound measurements are ± 0.5 kg m^{-3} and 0.1 m s^{-1}, respectively. Further, uncertainty in the temperature measurement is ± 0.01 K.

The molar heat capacities, C_P, of pure liquids and the present mixtures were measured by differential scanning calorimeter Micro DSC (Model—μDSC 7 Evo) manufactured by M/S SETARAM instrumentation, France, as described elsewhere [56]. The calibration of equipment was done by Joule effect method which in turn was controlled by SETARAM software. The joule effect calibration was checked by measuring heat of fusion of naphthalene (147.78 J g^{-1}) [57]. The heat capacity of a liquid or their mixtures was measured in a standard batch cell (Hastalloy C276) composed of a cylinder of 6.4 mm of internal diameter and 19.5 mm height and had a capacity of containing 1 cm^3 of a liquid. The reference experimental cell was filled with water (equivalent to the mass of liquid in a standard batch cell). The mole fraction of each mixture was made by measuring the masses of the components of mixtures in airtight glass bottles using an electric balance (Mettler AX-205 Delta) with an uncertainty of $\pm 10^{-5}$ g. For a scanning sequence, the initial and final temperatures were supplied along with heating rate of 0.4 K min^{-1}. The temperature cycle and scanning rate of isothermal level were maintained by software provided by SETARAM instrumentation. The uncertainty in measured heat capacity, C_P, values is 0.3 %.The uncertainty in mole fraction is 1×10^{-4}. The uncertainty in the temperature measurement is ± 0.02 K.

Results

The molar heat capacities, C_P, of [emim][BF_4] (1) + 2-Py or NMP (2) + cyclopentanone or cyclohexanone (3) ternary mixtures are listed in Table 3. The excess heat

Table 1 Details of studied chemicals, CAS number, source, purification method, purity and analysis method

Chemical name	CAS number	Source	Purification method	Purity	Analysis method
1-Ethyl-3-methyl imidazolium tetrafluoroborate	143314-16-3	Fluka	Used as such	0.980	GC
Pyrrolidin-2-one	616-45-5	Fluka	Vacuum distillation	0.994	GC
1-Methyl pyrrolidin-2-one	872-50-4	Fluka	Vacuum distillation	0.992	GC
Cyclopentanone	120-92-3	Fluka	Fractional distillation	0.991	GC
Cyclohexanone	108-94-1	Fluka	Fractional distillation	0.988	GC

GC Gas chromatography

Table 2 Comparison of densities, ρ, speeds of sound, u, and heat capacities, C_P, of pure liquids with their literature values at $T = (293.15$ to $308.15)$ K

Liquids	T/K	ρ/kg m^{-3}		u/m s^{-1}		C_P/J K^{-1} mol^{-1}	
		(Expt.)	(Lit.)	(Expt.)	(Lit.)	(Expt.)	(Lit.)
1-Ethyl-3-methylimidazolium tetrafluoroborate	293.15	1,283.9	1,284.30[a]	1,631.1	–	303.16	303.2[u]
	298.15	1,280.0	1,279.60[b]	1,619.6	–	304.63	304.9[u]
			1,280.07[c]				
	303.15	1,276.3	1,276.50[a]	1,608.1	–	306.21	306.6[u]
			1,275.70[b]				
	308.15	1,272.1	1,271.90[b]	1,596.6	–	307.83	308.4[u]
			1,272.48[c]				
Pyrrolidin-2-one	293.15	1,111.3	1,111.28[d]	1,651.09	1,650.13[d]	168.53	–
	298.15	1,107.2	1,107.15[d]	1,634.29	1,633.92[d]	169.99	169.37[f]
			1,107.20[e]		1,633.95[f]		
	303.15	1,103.1	1,103.02[d]	1,617.71	1,617.14[d]	171.33	–
			1,103.37[f]		1,617.61[f]		
	308.15	1,098.9	1,098.90[d]	1,602.32	1,601.85[d]	172.57	–
					1,601.87[f]		
1-Methyl pyrrolidin-2-one	293.15	1,033.2	1,032.87[g]	1,565.65	1,565.50[g]	165.59	–
			1,033.23[f]				
	298.15	1,028.2	1,028.23[f]	1,546.15	1,546.06[r]	166.35	166.1[v]
	303.15	1,023.5	1,023.40[h]	1,527.32	1,527.24[d]	167.08	–
			1,023.47[i]				
	308.15	1,018.7	1,018.66[d]	1,507.56	1,507.41[d]	167.53	–
Cyclopentanone	293.15	949.34	–	1,414.3	–	152.99	–
	298.15	944.52	944.35[j]	1,393.2	1,394.1[s]	154.69	154.5[v]
			945.30[k]				
	303.15	939.68	–	1,372.5	–	155.74	–
	308.15	934.84	–	1,352.6	–	156.81	–
Cyclohexanone	293.15	947.39	946.44[l]	1,431.9	1,430.5[t]	176.19	–
			947.80[m]				
	298.15	942.90	942.4[n]	1,414.8	1,408.0[s]	178.37	177.97[w]
			942.76[o]		1,417.0[n]		
	303.15	938.05	937.4[p]	1,395.6	–	180.46	–
			940.3[q]				
	308.15	933.18	933.8[o]	1,375.8	–	182.39	–

Standard uncertainties, u, are u (T) (DSA) $= \pm 0.01$ K; u $(\rho) = \pm 0.5$ kg m^{-3}; u $(u) = \pm 0.1$ m s^{-1}, u $(C_P) = 0.3$ %; u (T) (DSC) $= \pm 0.02$ K. [o] Ref. [23], [q] Ref. [25], [v] Ref. [33], [a] Ref. [34], [b] Ref. [35], [c] Ref. [36], [d] Ref. [37], [e] Ref. [38], [f] Ref. [39], [g] Ref. [40], [h] Ref. [41], [i] Ref. [42], [j] Ref. [43], [k] Ref. [44], [l] Ref. [45], [m] Ref. [46], [n] Ref. [47], [p] Ref. [48], [r] Ref. [49], [s] Ref. [50], [t] Ref. [51], [u] Ref. [52], [w] Ref. [53]

capacities, $(C_P^E)_{123}$, for $(1 + 2 + 3)$ mixtures were calculated by Eq. 1

$$(C_P^E)_{123} = (C_P) - \sum_{i=1}^{3} x_i (C_P)_i \tag{1}$$

where (C_P), $(C_P)_i$ $(i = 1$ or 2 or 3) and x_i $(i = 1$ or 2 or 3) denote molar heat capacity of the ternary mixtures, molar heat capacity and mole fraction of pure components, respectively. Such $(C_P^E)_{123}$ values for the present $(1 + 2 + 3)$ mixtures are listed in Table 3. The $(C_P^E)_{123}$ were fitted to Redlich–Kister [58] equation

$$\begin{aligned}(C_P^E)_{123} = {} & x_1 x_2 \left[\sum_{n=0}^{2} (C_P)_{12}^{(n)} (x_1 - x_2)^n\right] \\ & + x_2 x_3 \left[\sum_{n=0}^{2} (C_P)_{23}^{(n)} (x_2 - x_3)^n\right] \\ & + x_1 x_3 \left[\sum_{n=0}^{2} (C_P)_{13}^{(n)} (x_3 - x_1)^n\right] \\ & + x_1 x_2 x_3 \left[\sum_{n=0}^{2} (C_P)_{123}^{(n)} (x_2 - x_3)^n x_1^n\right]\end{aligned} \tag{2}$$

Table 3 Comparison of experimental $(C_P)_{123}$ data for the various (1 + 2 + 3) ternary mixtures with values evaluated from the Graph and Flory theories at $T = (293.15–308.15)$ K

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
1-Ethyl-3-methylimidazolium tetrafluoroborate (1) + pyrrolidin-2-one (2) + cyclopentanone (3)					
T/K = 293.15					
0.0976	0.8597	183.62	2.61	2.10	0.30
0.1093	0.8433	185.51	3.00	2.35	0.32
0.1214	0.8255	187.50	3.45	2.72	0.35
0.1431	0.7822	191.41	4.78	4.77	0.41
0.1678	0.7486	195.57	5.75	5.22	0.46
0.1842	0.7109	198.76	7.06	7.31	0.52
0.2013	0.6856	201.71	7.84	7.84	0.56
0.2208	0.6602	204.97	8.56	8.06	0.61
0.2532	0.6133	210.34	9.80	8.94	0.69
0.2734	0.5765	213.67	10.66	10.21	0.76
0.3006	0.5337	217.76	11.34	11.12	0.84
0.3245	0.5008	221.09	11.59	11.41	0.90
0.3605	0.4532	225.74	11.57	11.57	1.00
0.3976	0.4132	230.22	11.10	10.97	1.07
0.4221	0.3945	233.15	10.64	10.08	1.10
0.4414	0.3701	235.24	10.21	9.99	1.15
0.4676	0.3511	238.23	9.56	9.04	1.17
0.4867	0.2121	238.74	9.37	10.73	1.20
0.5006	0.3177	241.73	8.63	8.38	1.22
0.5367	0.2954	245.75	7.57	7.06	1.21
0.5689	0.1856	248.46	7.15	6.98	1.32
0.5822	0.2476	250.48	6.21	6.12	1.27
0.6004	0.2309	252.43	5.69	5.75	1.26
0.6429	0.2108	257.19	4.38	4.39	1.22
0.6676	0.2001	259.97	3.62	3.67	1.17
0.6846	0.1693	261.86	3.43	3.43	1.24
0.7113	0.1432	264.98	2.95	2.66	1.25
0.7324	0.1212	267.54	2.68	1.89	1.26
0.7478	0.1097	269.41	2.42	1.40	1.25
0.7864	0.0965	274.07	1.49	0.83	1.11
0.8006	0.0865	275.88	1.32	0.47	1.09
0.8234	0.0835	278.67	0.73	0.46	0.97
T/K = 298.15					
0.0976	0.8597	185.26	2.78	2.25	0.73
0.1093	0.8433	187.16	3.18	2.52	0.79
0.1214	0.8255	189.18	3.66	2.91	0.80
0.1431	0.7822	193.19	5.08	5.07	0.85
0.1678	0.7486	197.41	6.11	5.56	0.96
0.1842	0.7109	200.69	7.50	7.76	1.08
0.2013	0.6856	203.69	8.33	8.33	1.16
0.2208	0.6602	206.99	9.09	8.58	1.23
0.2532	0.6133	212.45	10.41	9.51	1.36
0.2734	0.5765	215.83	11.33	10.86	1.45
0.3006	0.5337	219.99	12.06	11.83	1.53

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.3245	0.5008	223.35	12.34	12.15	1.58
0.3605	0.4532	228.01	12.33	12.33	1.70
0.3976	0.4132	232.49	11.86	11.75	1.84
0.4221	0.3945	235.41	11.39	11.71	1.87
0.4414	0.3701	237.47	10.93	10.78	1.90
0.4676	0.3511	240.43	10.26	10.69	1.97
0.4867	0.2121	240.52	9.61	9.70	1.99
0.5006	0.3177	243.90	9.29	11.42	2.00
0.5367	0.2954	247.86	8.18	9.01	2.02
0.5689	0.1856	250.24	7.41	7.63	2.03
0.5822	0.2476	252.49	6.72	7.47	2.01
0.6004	0.2309	254.41	6.16	6.56	1.97
0.6429	0.2108	259.13	4.82	6.23	1.93
0.6676	0.2001	261.87	4.02	4.80	1.87
0.6846	0.1693	263.69	3.76	4.05	1.86
0.7113	0.1432	266.75	3.22	3.76	1.81
0.7324	0.1212	269.25	2.89	2.92	1.76
0.7478	0.1097	271.10	2.61	2.09	1.71
0.7864	0.0965	275.76	1.68	1.56	1.54
0.8006	0.0865	277.54	1.48	0.96	1.48
0.8234	0.0835	280.32	0.89	0.56	1.35
T/K = 303.15					
0.0976	0.8597	186.84	3.01	2.74	0.67
0.1093	0.8433	188.76	3.43	3.05	0.72
0.1214	0.8255	190.81	3.93	3.47	0.73
0.1431	0.7822	194.88	5.41	5.51	0.78
0.1678	0.7486	199.12	6.46	6.06	0.88
0.1842	0.7109	202.44	7.90	8.15	0.98
0.2013	0.6856	205.46	8.74	8.74	1.05
0.2208	0.6602	208.78	9.52	9.04	1.12
0.2532	0.6133	214.27	10.87	10.01	1.23
0.2734	0.5765	217.70	11.83	11.35	1.32
0.3006	0.5337	221.90	12.61	12.36	1.39
0.3245	0.5008	225.30	12.93	12.72	1.44
0.3605	0.4532	230.03	12.98	12.98	1.56
0.3976	0.4132	234.55	12.54	12.41	1.69
0.4221	0.3945	237.45	12.05	11.48	1.72
0.4414	0.3701	239.56	11.63	11.41	1.75
0.4676	0.3511	242.51	10.94	10.41	1.82
0.4867	0.2121	242.58	10.30	11.99	1.83
0.5006	0.3177	246.00	9.98	9.72	1.85
0.5367	0.2954	249.93	8.83	8.28	1.87
0.5689	0.1856	252.28	8.04	7.99	1.88
0.5822	0.2476	254.56	7.36	7.06	1.85
0.6004	0.2309	256.47	6.79	6.86	1.88
0.6429	0.2108	261.14	5.38	5.33	1.84
0.6676	0.2001	263.85	4.54	4.52	1.80

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.6846	0.1693	265.66	4.27	4.27	1.75
0.7113	0.1432	268.68	3.68	3.42	1.75
0.7324	0.1212	271.14	3.31	2.58	1.71
0.7478	0.1097	272.97	3.00	2.02	1.67
0.7864	0.0965	277.58	2.01	1.26	1.63
0.8006	0.0865	279.34	1.79	0.82	1.47
0.8234	0.0835	282.10	1.16	0.83	1.29
T/K = 308.15					
0.0976	0.8597	188.22	3.12	2.80	0.66
0.1093	0.8433	190.16	3.55	3.13	0.71
0.1214	0.8255	192.19	4.04	3.56	0.72
0.1431	0.7822	196.28	5.53	5.56	0.76
0.1678	0.7486	200.50	6.55	6.16	0.86
0.1842	0.7109	203.82	7.99	8.20	0.96
0.2013	0.6856	206.83	8.81	8.81	1.03
0.2208	0.6602	210.11	9.55	9.15	1.09
0.2532	0.6133	215.59	10.88	10.16	1.20
0.2734	0.5765	219.05	11.87	11.49	1.28
0.3006	0.5337	223.32	12.70	12.52	1.35
0.3245	0.5008	226.77	13.06	12.91	1.40
0.3605	0.4532	231.61	13.21	13.21	1.52
0.3976	0.4132	236.20	12.83	12.71	1.65
0.4221	0.3945	239.11	12.34	11.85	1.67
0.4414	0.3701	241.29	11.99	11.78	1.70
0.4676	0.3511	244.26	11.30	10.85	1.77
0.4867	0.2121	244.50	10.85	11.99	1.78
0.5006	0.3177	247.83	10.41	10.18	1.79
0.5367	0.2954	251.76	9.24	8.82	1.81
0.5689	0.1856	254.19	8.54	8.09	1.83
0.5822	0.2476	256.49	7.85	7.18	1.82
0.6004	0.2309	258.40	7.28	7.33	1.83
0.6429	0.2108	263.02	5.80	5.87	1.76
0.6676	0.2001	265.70	4.92	5.11	1.70
0.6846	0.1693	267.55	4.68	4.68	1.71
0.7113	0.1432	270.54	4.05	3.72	1.69
0.7324	0.1212	272.96	3.63	2.76	1.63
0.7478	0.1097	274.75	3.28	2.16	1.59
0.7864	0.0965	279.34	2.25	1.43	1.44
0.8006	0.0865	281.08	2.00	0.95	1.39
0.8234	0.0835	283.84	1.36	1.03	2.06
1-Ethyl-3-methylimidazolium tetrafluoroborate (1) + pyrrolidin-2-one (2) + cyclohexanone (3)					
T/K = 293.15					
0.0963	0.8498	184.03	3.37	3.74	0.39
0.1154	0.8317	186.92	3.68	3.19	0.42
0.1265	0.8103	188.88	4.30	4.15	0.46
0.1467	0.7854	192.09	4.86	4.28	0.50
0.1612	0.7609	194.59	5.57	5.00	0.54

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.1821	0.7256	198.18	6.57	6.03	0.61
0.1955	0.6932	200.73	7.61	7.61	0.67
0.2166	0.6636	204.12	8.29	7.97	0.72
0.2361	0.6389	207.14	8.77	8.01	0.77
0.2598	0.5999	210.89	9.56	8.94	0.85
0.2713	0.5808	212.64	9.88	9.42	0.88
0.3002	0.5365	216.78	10.37	10.06	0.97
0.3196	0.5122	219.37	10.43	10.00	1.02
0.3287	0.4899	220.53	10.57	10.75	1.07
0.3478	0.4638	222.88	10.45	10.75	1.13
0.3611	0.4521	224.50	10.26	10.30	1.15
0.3814	0.4292	226.87	9.94	9.94	1.19
0.3936	0.4105	228.18	9.70	10.04	1.23
0.4135	0.3989	230.54	9.26	9.00	1.24
0.4332	0.3834	232.77	8.77	8.29	1.26
0.4589	0.3512	235.38	8.02	7.90	1.32
0.4832	0.3362	238.10	7.32	6.89	1.32
0.5098	0.2761	239.90	6.06	6.93	1.47
0.5386	0.2963	244.06	5.58	5.02	1.32
0.5521	0.2045	246.12	4.10	4.83	1.32
0.5846	0.2424	248.47	3.92	3.92	1.64
0.6044	0.2315	250.68	3.33	3.29	1.40
0.6256	0.2233	253.15	2.74	2.65	1.38
0.6461	0.2169	255.57	2.18	2.10	1.34
0.6647	0.2071	257.69	1.66	1.66	1.28
0.6812	0.1653	259.87	1.02	0.94	1.25
0.7143	0.1476	263.88	0.28	0.20	1.37
T/K = 298.15					
0.0963	0.8498	186.90	3.49	3.86	0.79
0.1154	0.8317	189.78	3.81	3.43	0.89
0.1265	0.8103	192.01	4.46	4.29	0.95
0.1467	0.7854	195.36	5.05	4.44	1.05
0.1612	0.7609	198.14	5.79	5.21	1.12
0.1821	0.7256	202.13	6.85	6.29	1.23
0.1955	0.6932	205.18	7.94	7.94	1.30
0.2166	0.6636	208.83	8.67	8.38	1.39
0.2361	0.6389	212.01	9.18	8.52	1.47
0.2598	0.5999	216.19	10.04	9.49	1.57
0.2713	0.5808	218.15	10.39	9.94	1.62
0.3002	0.5365	222.74	10.96	10.67	1.72
0.3196	0.5122	225.48	11.05	10.64	1.79
0.3287	0.4899	227.02	11.25	11.45	1.83
0.3478	0.4638	229.58	11.18	11.49	1.88
0.3611	0.4521	231.17	11.00	11.05	1.91
0.3814	0.4292	233.64	10.71	10.71	1.96
0.3936	0.4105	235.14	10.51	10.79	1.99
0.4135	0.3989	237.29	10.05	9.80	2.03

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.4332	0.3834	239.42	9.57	9.08	2.05
0.4589	0.3512	242.23	8.86	8.73	2.09
0.4832	0.3362	244.71	8.15	7.71	2.10
0.5098	0.2761	247.38	6.96	7.85	2.16
0.5386	0.2963	250.28	6.39	5.82	2.10
0.5521	0.2045	251.24	4.88	5.81	2.22
0.5846	0.2424	254.90	4.75	4.75	2.10
0.6044	0.2315	256.88	4.14	4.09	2.07
0.6256	0.2233	259.01	3.52	3.42	2.02
0.6461	0.2169	261.05	2.92	2.83	1.97
0.6647	0.2071	262.93	2.37	2.37	1.92
0.6812	0.1653	264.74	1.75	1.68	1.94
0.7143	0.1476	268.28	0.96	0.89	1.84
T/K = 303.15					
0.0963	0.8498	188.66	3.85	4.32	0.75
0.1154	0.8317	191.61	4.23	3.86	0.84
0.1265	0.8103	193.94	4.97	4.84	0.90
0.1467	0.7854	197.41	5.67	5.03	0.99
0.1612	0.7609	200.31	6.53	5.91	1.06
0.1821	0.7256	204.51	7.78	7.17	1.16
0.1955	0.6932	207.76	9.04	9.04	1.24
0.2166	0.6636	211.57	9.93	9.58	1.33
0.2361	0.6389	214.89	10.57	9.77	1.41
0.2598	0.5999	219.25	11.60	10.91	1.51
0.2713	0.5808	221.30	12.03	11.45	1.55
0.3002	0.5365	226.03	12.72	12.32	1.66
0.3196	0.5122	228.83	12.86	12.33	1.73
0.3287	0.4899	230.38	13.06	13.25	1.77
0.3478	0.4638	232.95	12.99	13.33	1.83
0.3611	0.4521	234.56	12.82	12.86	1.86
0.3814	0.4292	237.01	12.51	12.51	1.91
0.3936	0.4105	238.48	12.27	12.61	1.95
0.4135	0.3989	240.63	11.81	11.52	1.97
0.4332	0.3834	242.72	11.29	10.74	2.00
0.4589	0.3512	245.43	10.47	10.37	2.05
0.4832	0.3362	247.86	9.71	9.25	2.06
0.5098	0.2761	250.32	8.27	9.34	2.15
0.5386	0.2963	253.26	7.78	7.16	2.06
0.5521	0.2045	254.02	6.00	6.90	2.24
0.5846	0.2424	257.65	5.89	5.89	2.08
0.6044	0.2315	259.57	5.22	5.15	2.05
0.6256	0.2233	261.63	4.54	4.42	2.00
0.6461	0.2169	263.62	3.89	3.79	1.94
0.6647	0.2071	265.44	3.28	3.28	1.90
0.6812	0.1653	267.15	2.54	2.30	1.94
0.7143	0.1476	270.59	1.65	1.38	1.84

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
T/K = 308.15					
0.0963	0.8498	190.19	4.07	4.57	0.75
0.1154	0.8317	193.18	4.48	4.09	0.84
0.1265	0.8103	195.58	5.28	5.13	0.87
0.1467	0.7854	199.11	6.03	5.35	0.98
0.1612	0.7609	202.09	6.95	6.30	1.05
0.1821	0.7256	206.40	8.29	7.65	1.15
0.1955	0.6932	209.76	9.65	9.65	1.22
0.2166	0.6636	213.66	10.62	10.24	1.31
0.2361	0.6389	217.05	11.32	10.47	1.38
0.2598	0.5999	221.54	12.45	11.71	1.48
0.2713	0.5808	223.63	12.91	12.29	1.53
0.3002	0.5365	228.47	13.69	13.25	1.63
0.3196	0.5122	231.31	13.86	13.29	1.69
0.3287	0.4899	232.90	14.09	14.29	1.74
0.3478	0.4638	235.49	14.03	14.39	1.80
0.3611	0.4521	237.12	13.87	13.90	1.82
0.3814	0.4292	239.57	13.55	13.55	1.87
0.3936	0.4105	241.04	13.31	13.68	1.91
0.4135	0.3989	243.18	12.84	12.54	1.93
0.4332	0.3834	245.28	12.31	11.73	1.96
0.4589	0.3512	247.97	11.46	11.35	2.00
0.4832	0.3362	250.37	10.67	10.18	2.01
0.5098	0.2761	252.79	9.16	10.30	2.10
0.5386	0.2963	255.69	8.65	7.99	2.01
0.5521	0.2045	256.41	6.77	7.74	2.19
0.5846	0.2424	260.00	6.66	6.66	2.03
0.6044	0.2315	261.88	5.95	5.87	2.00
0.6256	0.2233	263.90	5.23	5.10	1.96
0.6461	0.2169	265.85	4.54	4.43	1.90
0.6647	0.2071	267.63	3.89	3.89	1.86
0.6812	0.1653	269.32	3.10	2.81	1.90
0.7143	0.1476	272.68	2.14	1.82	1.81
1-Ethyl-3-methylimidazolium tetrafluoroborate (1) + 1-methyl pyrrolidin-2-one (2) + cyclopentanone (3)					
T/K = 293.15					
0.0967	0.7769	180.80	3.50	3.04	0.46
0.1124	0.7434	183.58	4.34	4.99	0.50
0.1313	0.7132	186.78	5.09	4.87	0.55
0.1509	0.6823	190.13	5.88	5.34	0.60
0.1611	0.6656	191.87	6.30	6.01	0.62
0.1710	0.6494	193.55	6.70	6.97	0.65
0.1823	0.6327	195.44	7.10	7.61	0.68
0.1925	0.6205	197.09	7.37	7.37	0.70
0.2028	0.6080	198.75	7.64	7.35	0.73
0.2234	0.5821	202.04	8.17	8.08	0.78
0.2307	0.5743	203.18	8.31	7.97	0.79
0.2412	0.5618	204.81	8.52	8.43	0.82

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.2623	0.5403	208.02	8.83	8.34	0.86
0.2865	0.5134	211.62	9.14	9.80	0.91
0.3312	0.4743	218.02	9.32	9.54	0.99
0.3487	0.4607	220.46	9.30	9.07	1.01
0.3612	0.4501	222.17	9.27	9.27	1.03
0.3771	0.4367	224.31	9.19	9.64	1.05
0.4012	0.4189	227.53	9.01	9.19	1.08
0.4389	0.3912	232.42	8.59	8.91	1.12
0.4534	0.3821	234.28	8.39	8.03	1.13
0.4698	0.3699	236.34	8.14	8.22	1.13
0.4878	0.3584	238.60	7.84	7.35	1.13
0.5011	0.3493	240.24	7.60	7.11	1.14
0.5213	0.3347	242.71	7.22	7.32	1.13
0.5418	0.3218	245.20	6.79	6.31	1.12
0.5754	0.2987	249.23	6.07	6.07	1.11
0.5912	0.2887	251.12	5.71	5.34	1.10
0.6076	0.2767	253.06	5.34	5.80	1.09
0.6287	0.2643	255.56	4.83	4.05	1.08
0.6454	0.2519	257.53	4.45	4.68	1.05
0.6898	0.2225	262.80	3.42	3.42	1.03
T/K = 298.15					
0.0967	0.7769	181.67	3.42	2.92	0.84
0.1124	0.7434	184.41	4.20	4.76	0.91
0.1313	0.7132	187.57	4.88	4.64	1.00
0.1509	0.6823	190.86	5.59	5.06	1.09
0.1611	0.6656	192.58	5.97	5.74	1.14
0.1710	0.6494	194.24	6.34	6.58	1.19
0.1823	0.6327	196.09	6.69	7.17	1.23
0.1925	0.6205	197.72	6.93	6.93	1.28
0.2028	0.6080	199.36	7.17	6.89	1.32
0.2234	0.5821	202.60	7.63	7.56	1.40
0.2307	0.5743	203.73	7.75	7.44	1.43
0.2412	0.5618	205.34	7.93	7.85	1.47
0.2623	0.5403	208.51	8.19	7.74	1.54
0.2865	0.5134	212.09	8.46	9.09	1.63
0.3312	0.4743	218.45	8.57	8.79	1.76
0.3487	0.4607	220.88	8.53	8.31	1.80
0.3612	0.4501	222.59	8.49	8.49	1.83
0.3771	0.4367	224.73	8.41	8.83	1.86
0.4012	0.4189	227.95	8.22	8.39	1.91
0.4389	0.3912	232.86	7.80	8.10	1.96
0.4534	0.3821	234.73	7.60	7.26	1.97
0.4698	0.3699	236.81	7.37	7.43	1.99
0.4878	0.3584	239.08	7.07	6.61	2.00
0.5011	0.3493	240.74	6.84	6.39	2.00
0.5213	0.3347	243.25	6.49	6.59	2.02
0.5418	0.3218	245.77	6.09	5.65	2.03

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.5754	0.2987	249.88	5.43	5.43	1.98
0.5912	0.2887	251.79	5.09	4.75	1.96
0.6076	0.2767	253.78	4.76	5.19	1.95
0.6287	0.2643	256.33	4.29	3.57	1.91
0.6454	0.2519	258.36	3.96	4.17	1.89
0.6898	0.2225	263.74	3.03	3.03	1.79
T/K = 303.15					
0.0967	0.7769	182.50	3.40	2.90	0.80
0.1124	0.7434	185.24	4.16	4.70	0.87
0.1313	0.7132	188.41	4.83	4.58	0.95
0.1509	0.6823	191.69	5.51	4.99	1.03
0.1611	0.6656	193.42	5.89	5.66	1.08
0.1710	0.6494	195.07	6.24	6.48	1.12
0.1823	0.6327	196.94	6.59	7.06	1.16
0.1925	0.6205	198.56	6.82	6.82	1.20
0.2028	0.6080	200.20	7.05	6.78	1.24
0.2234	0.5821	203.45	7.49	7.43	1.32
0.2307	0.5743	204.58	7.61	7.31	1.34
0.2412	0.5618	206.19	7.79	7.71	1.38
0.2623	0.5403	209.38	8.04	7.60	1.45
0.2865	0.5134	212.97	8.30	8.91	1.53
0.3312	0.4743	219.35	8.40	8.61	1.65
0.3487	0.4607	221.78	8.35	8.14	1.69
0.3612	0.4501	223.50	8.31	8.31	1.71
0.3771	0.4367	225.66	8.23	8.63	1.74
0.4012	0.4189	228.90	8.04	8.20	1.78
0.4389	0.3912	233.85	7.63	7.91	1.83
0.4534	0.3821	235.72	7.42	7.09	1.85
0.4698	0.3699	237.82	7.19	7.26	1.86
0.4878	0.3584	240.10	6.90	6.45	1.87
0.5011	0.3493	241.78	6.68	6.23	1.87
0.5213	0.3347	244.31	6.33	6.42	1.88
0.5418	0.3218	246.85	5.94	5.50	1.87
0.5754	0.2987	250.99	5.28	5.28	1.86
0.5912	0.2887	252.92	4.95	4.62	1.84
0.6076	0.2767	254.93	4.63	5.05	1.83
0.6287	0.2643	257.51	4.17	3.46	1.80
0.6454	0.2519	259.55	3.84	4.05	1.77
0.6898	0.2225	264.99	2.93	2.93	1.69
T/K = 308.15					
0.0967	0.7769	183.06	3.32	2.82	0.79
0.1124	0.7434	185.77	4.02	4.47	0.86
0.1313	0.7132	188.89	4.61	4.36	0.94
0.1509	0.6823	192.13	5.22	4.73	1.02
0.1611	0.6656	193.82	5.55	5.33	1.06
0.1710	0.6494	195.47	5.87	6.07	1.10
0.1823	0.6327	197.29	6.17	6.59	1.15

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.1925	0.6205	198.89	6.36	6.36	1.19
0.2028	0.6080	200.51	6.56	6.32	1.22
0.2234	0.5821	203.73	6.94	6.88	1.30
0.2307	0.5743	204.84	7.03	6.77	1.32
0.2412	0.5618	206.45	7.19	7.12	1.36
0.2623	0.5403	209.49	7.28	6.84	1.42
0.2865	0.5134	212.96	7.38	7.00	1.50
0.3312	0.4743	219.51	7.60	8.15	1.62
0.3487	0.4607	222.05	7.64	7.82	1.65
0.3612	0.4501	223.75	7.57	7.38	1.68
0.3771	0.4367	225.96	7.52	7.52	1.71
0.4012	0.4189	229.33	7.44	7.80	1.75
0.4389	0.3912	234.53	7.24	7.38	1.80
0.4534	0.3821	236.22	6.84	7.09	1.81
0.4698	0.3699	238.36	6.64	6.34	1.82
0.4878	0.3584	240.75	6.43	6.48	1.83
0.5011	0.3493	242.38	6.15	5.75	1.84
0.5213	0.3347	245.06	5.94	5.54	1.84
0.5418	0.3218	247.71	5.63	5.71	1.83
0.5754	0.2987	252.17	5.26	4.87	1.82
0.5912	0.2887	253.86	4.67	4.67	1.81
0.6076	0.2767	255.91	4.37	4.08	1.79
0.6287	0.2643	258.68	4.09	4.46	1.76
0.6454	0.2519	260.64	3.66	3.04	1.74
0.6898	0.2225	266.75	3.38	3.57	1.66
1-Ethyl-3-methylimidazolium tetrafluoroborate (1) + 1-methyl pyrrolidin-2-one (2) + cyclohexanone (3)					
T/K = 293.15					
0.1004	0.8533	181.23	1.34	1.24	0.31
0.1221	0.8201	184.99	1.99	1.84	0.35
0.1439	0.7820	189.13	2.96	2.88	0.40
0.1636	0.7511	192.76	3.76	3.58	0.44
0.1809	0.7266	195.85	4.39	4.01	0.47
0.1913	0.7012	198.25	5.20	5.10	0.51
0.2002	0.6838	200.07	5.71	5.71	0.54
0.2216	0.6617	203.48	6.17	5.58	0.57
0.2434	0.6279	207.43	6.99	6.31	0.63
0.2645	0.5897	211.31	7.79	7.35	0.70
0.2723	0.5743	212.73	8.05	7.79	0.73
0.2971	0.5417	216.58	8.41	8.00	0.79
0.3302	0.5005	221.38	8.57	8.02	0.86
0.3601	0.4519	225.45	8.33	8.33	1.00
0.3724	0.4411	227.00	8.20	8.00	0.98
0.3865	0.4246	228.73	7.97	7.75	1.02
0.3975	0.4201	230.10	7.89	7.34	1.01
0.4098	0.4004	231.51	7.53	7.18	1.06
0.4259	0.3734	233.22	6.91	6.81	1.12
0.4349	0.3605	234.16	6.57	6.50	1.15

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.4501	0.3334	235.59	5.78	5.78	1.22
0.4634	0.3253	237.13	5.55	5.21	1.23
0.4722	0.3054	237.81	4.90	4.50	1.29
0.4809	0.2912	238.59	4.43	3.80	1.33
0.5710	0.2889	249.98	4.35	4.03	1.10
0.5835	0.2833	251.41	4.14	4.14	1.08
0.6089	0.2653	254.23	3.54	3.91	1.07
0.6335	0.2456	256.93	2.91	3.44	1.06
0.6643	0.2203	260.34	2.14	2.66	1.06
0.6817	0.2034	262.26	1.67	1.77	1.07
0.7007	0.1923	264.47	1.35	1.82	1.04
0.7123	0.1805	265.77	1.05	1.04	1.04
T/K = 298.15					
0.1004	0.8533	182.11	1.32	1.30	0.74
0.1221	0.8201	185.85	1.92	1.89	0.84
0.1439	0.7820	189.96	2.82	2.83	0.94
0.1636	0.7511	193.55	3.55	3.45	1.03
0.1809	0.7266	196.60	4.12	3.83	1.10
0.1913	0.7012	198.97	4.87	4.79	1.15
0.2002	0.6838	200.75	5.32	5.32	1.19
0.2216	0.6617	204.13	5.73	5.21	1.27
0.2434	0.6279	208.01	6.46	5.85	1.35
0.2645	0.5897	211.85	7.17	6.74	1.44
0.2723	0.5743	213.24	7.39	7.12	1.47
0.2971	0.5417	217.05	7.68	7.29	1.55
0.3302	0.5005	221.83	7.78	7.27	1.65
0.3601	0.4519	225.89	7.49	7.49	1.75
0.3724	0.4411	227.46	7.37	7.20	1.77
0.3865	0.4246	229.20	7.13	6.96	1.81
0.3975	0.4201	230.57	7.06	6.59	1.82
0.4098	0.4004	232.01	6.71	6.43	1.85
0.4259	0.3734	233.79	6.13	6.07	1.90
0.4349	0.3605	234.77	5.82	5.78	1.92
0.4501	0.3334	236.30	5.11	5.11	1.96
0.4634	0.3253	237.86	4.89	4.60	1.97
0.4722	0.3054	238.66	4.34	3.95	2.00
0.4809	0.2912	239.53	3.94	3.31	2.02
0.5710	0.2889	250.78	3.79	3.51	1.90
0.5835	0.2833	252.24	3.60	3.60	1.89
0.6089	0.2653	255.12	3.06	3.37	1.86
0.6335	0.2456	257.90	2.50	2.94	1.83
0.6643	0.2203	261.43	1.83	2.23	1.78
0.6817	0.2034	263.41	1.41	1.44	1.76
0.7007	0.1923	265.67	1.14	1.48	1.71
0.7123	0.1805	267.03	0.89	0.78	1.69
T/K = 303.15					
0.1004	0.8533	182.89	1.22	1.26	0.70

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.1221	0.8201	186.61	1.77	1.78	0.80
0.1439	0.7820	190.68	2.59	2.62	0.89
0.1636	0.7511	194.24	3.26	3.19	0.97
0.1809	0.7266	197.26	3.77	3.54	1.04
0.1913	0.7012	199.60	4.47	4.41	1.10
0.2002	0.6838	201.38	4.89	4.89	1.14
0.2216	0.6617	204.71	5.24	4.78	1.21
0.2434	0.6279	208.57	5.90	5.35	1.29
0.2645	0.5897	212.37	6.54	6.15	1.38
0.2723	0.5743	213.76	6.74	6.49	1.41
0.2971	0.5417	217.56	6.99	6.63	1.49
0.3302	0.5005	222.34	7.05	6.59	1.60
0.3601	0.4519	226.47	6.77	6.77	1.70
0.3724	0.4411	228.03	6.64	6.49	1.73
0.3865	0.4246	229.80	6.42	6.26	1.76
0.3975	0.4201	231.16	6.34	5.92	1.77
0.4098	0.4004	232.64	6.01	5.77	1.81
0.4259	0.3734	234.50	5.48	5.43	1.86
0.4349	0.3605	235.52	5.19	5.16	1.89
0.4501	0.3334	237.15	4.55	4.55	1.94
0.4634	0.3253	238.72	4.34	4.08	1.95
0.4722	0.3054	239.61	3.86	3.49	2.01
0.4809	0.2912	240.54	3.50	2.91	1.86
0.5710	0.2889	251.66	3.26	3.01	1.84
0.5835	0.2833	253.13	3.09	3.09	1.81
0.6089	0.2653	256.07	2.59	2.87	1.79
0.6335	0.2456	258.93	2.09	2.47	1.75
0.6643	0.2203	262.53	1.48	1.83	1.73
0.6817	0.2034	264.57	1.11	1.11	1.68
0.7007	0.1923	266.86	0.86	1.14	1.66
0.7123	0.1805	268.26	0.64	0.51	1.65
T/K = 308.15					
0.1004	0.8533	183.45	1.15	1.26	0.69
0.1221	0.8201	187.19	1.67	1.76	0.79
0.1439	0.7820	191.29	2.47	2.56	0.88
0.1636	0.7511	194.86	3.11	3.10	0.96
0.1809	0.7266	197.89	3.61	3.42	1.03
0.1913	0.7012	200.25	4.28	4.24	1.08
0.2002	0.6838	202.03	4.69	4.69	1.12
0.2216	0.6617	205.38	5.03	4.58	1.18
0.2434	0.6279	209.26	5.67	5.11	1.27
0.2645	0.5897	213.08	6.27	5.84	1.35
0.2723	0.5743	214.45	6.44	6.15	1.38
0.2971	0.5417	218.27	6.66	6.26	1.46
0.3302	0.5005	223.05	6.68	6.20	1.56
0.3601	0.4519	227.17	6.32	6.32	1.66
0.3724	0.4411	228.74	6.19	6.04	1.69

Table 3 continued

x_1	x_2	$(C_P)_{123}$/J K^{-1} mol^{-1}	$(C_P^E)_{123}$/J K^{-1} mol^{-1}		
			(Expt.)	Graph	Flory
0.3865	0.4246	230.51	5.95	5.81	1.72
0.3975	0.4201	231.89	5.88	5.49	1.73
0.4098	0.4004	233.38	5.53	5.32	1.77
0.4259	0.3734	235.24	4.97	4.96	1.82
0.4349	0.3605	236.28	4.69	4.69	1.84
0.4501	0.3334	237.97	4.07	4.07	1.89
0.4634	0.3253	239.55	3.87	3.62	1.90
0.4722	0.3054	240.50	3.42	3.02	1.94
0.4809	0.2912	241.51	3.12	2.45	1.97
0.5710	0.2889	252.61	2.89	2.66	1.81
0.5835	0.2833	254.10	2.73	2.73	1.80
0.6089	0.2653	256.90	2.07	2.52	1.77
0.6335	0.2456	259.99	1.78	2.13	1.75
0.6643	0.2203	263.66	1.21	1.51	1.71
0.6817	0.2034	265.75	0.87	0.82	1.69
0.7007	0.1923	268.08	0.65	0.86	1.64
0.7123	0.1805	269.51	0.45	0.25	1.63

The standard uncertainty in the measured $\left(C_P^E\right)_{123}$ values is $u\left(C_P^E\right)_{123} = \pm 0.3$ % at 0.1 MPa

where $(C_P)_{123}^{(n)}(n = 0 - 2)$, etc., are characteristic parameters of binaries (1 + 2), (2 + 3) and (1 + 3) of (1 + 2 + 3) mixtures and were taken from literature [59–61]. The $(C_P)_{123}^{(n)}(n = 0 - 2)$, etc., are ternary adjustable parameters of the (1 + 2 + 3) ternary mixtures and were calculated by least-square optimization of these parameters. Such parameters along with standard deviations, $\sigma(C_P^E)_{123}$, defined by Eq. 3

$$\sigma\left((C_P^E)_{123}\right) = \left[\sum \left((C_P^E)_{123\{\exp tl\}} - (C_P^E)_{123\{calc.equation(2)\}}\right)^2 \Big/ (m-n)\right]^{0.5} \quad (3)$$

(where m is the number of data points and n is the number of adjustable parameters of Eq. 2) are listed in supporting Table 1S. Various surfaces generated by $(C_P^E)_{123}$ data are shown in Figs. 1–4. In Fig. 1, $(C_P^E)_{123}$ values (corresponding to 1–2 axis) were obtained by keeping x_3 constant and varying the values of x_1 and x_2 (shown as green line); $(C_P^E)_{123}$ values (corresponding to 1–3 axis) were obtained by keeping x_2 constant and varying the values x_1 and x_3 (shown as red line).

Discussion

The excess heat capacities, $(C_P^E)_{123}$, of the [emim][BF_4] (1) + NMP or 2-Py (2) + cyclopentanone or cyclohexanone (3) mixtures are not available in literature for comparison with measured results. The $(C_P^E)_{123}$ of the present (1 + 2 + 3) mixtures are positive over entire mole fraction of (1) and (2). The positive $(C_P^E)_{123}$ values suggest that capability of cyclohexanone or cyclopentanone molecules to build a non-random structure in mixed state (due to interactions with [emim][BF_4]:NMP or 2-Py molecular entities) is superior to the effect caused by disruption of associated NMP or 2-Py entities, and interactions between [emim][BF_4]:NMP or 2-Py molecular entities [37]. The $(C_P^E)_{123}$ values of [emim][BF_4] (1) + NMP or 2-Py (2) + cyclohexanone (3) mixtures are higher than those of [emim][BF_4] (1) + NMP or 2-Py (2) + cyclopentanone (3) mixtures. It may be due to reason that cyclohexanone is more basic in character than cyclopentanone [62] and also possesses chair form with almost no strain. Thus, cyclohexanone will give strong interactions and more compact structure with [emim][BF_4]: NMP or 2-Py molecular entities as compared to cyclopentanone. Higher$(C_P^E)_{123}$ for [emim][BF_4] (1) + 2-Py (2) + cyclopentanone or cyclohexanone (3) mixtures than those for [emim][BF_4] (1) + NMP (2) + cyclopentanone or cyclohexanone (3) mixtures may be due to lesser mixing of 2-Py with [emim][BF_4] and cyclohexanone because of the preference of 2-Py molecules to hydrogen bond with themselves. The $\left(\frac{\partial C_P^E}{\partial T}\right)$ for [emim][BF_4] (1) + 2-Py (2) + cyclopentanone or cyclohexanone (3) mixtures are positive which in turn

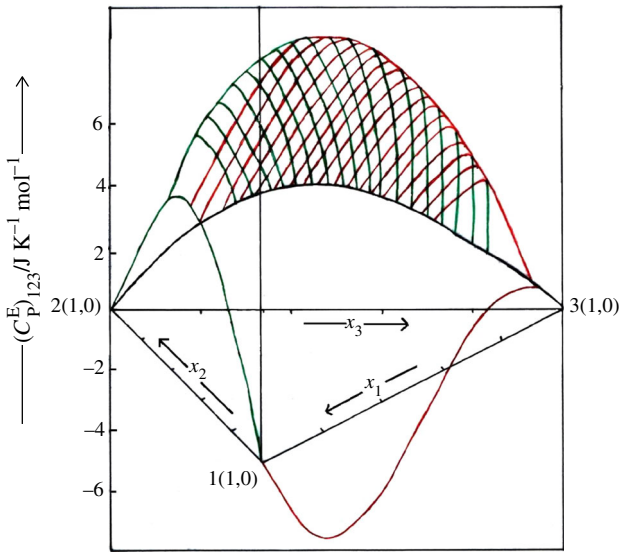

Fig. 1 Excess heat capacities, $(C_P^E)_{123}$, for 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + pyrrolidin-2-one (2) + cyclopentanone (3) mixture at 298.15 K. (Color figure online)

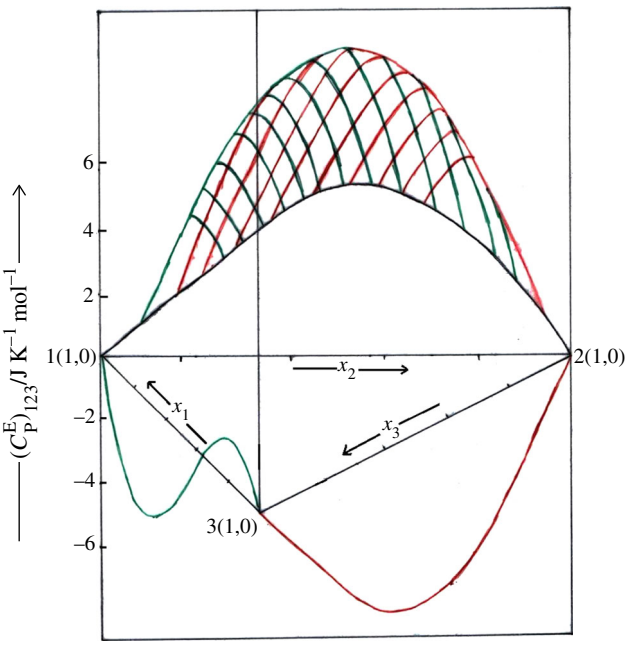

Fig. 2 Excess heat capacities, $(C_P^E)_{123}$, for 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + pyrrolidin-2-one (2) + cyclohexanone (3) mixture at 298.15 K. (Color figure online)

suggest strong interactions occurring in mixed state due to disruption of self-associated entities of 2-Py and ion–dipole interactions in [emim][BF_4]. However, $\left(\frac{\partial C_P^E}{\partial T}\right)$ for [emim][BF_4] (1) + NMP (2) + cyclopentanone or cyclohexanone (3) mixtures are negative. Decreasing $(C_P^E)_{123}$ values with increasing temperature can be associated with decrease of molecular interactions between like molecules compared with unlike molecules in mixed state.

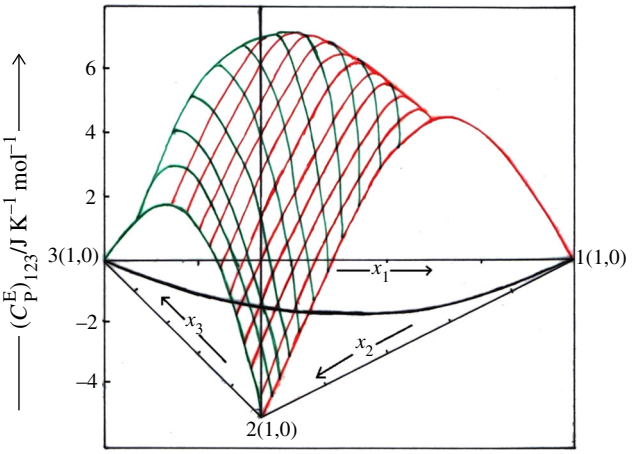

Fig. 3 Excess heat capacities, $(C_P^E)_{123}$, for 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + 1-methylpyrrolidin-2-one (2) + cyclopentanone (3) mixture at 298.15 K. (Color figure online)

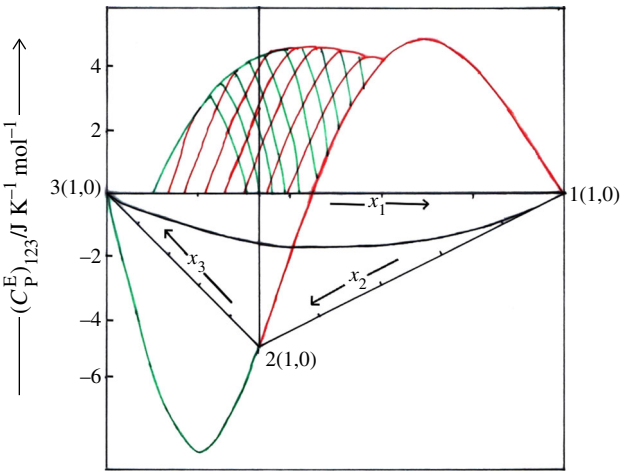

Fig. 4 Excess heat capacities, $(C_P^E)_{123}$, for 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + 1-methylpyrrolidin-2-one (2) + cyclohexanone (3) ternary mixture at 298.15 K. (Color figure online)

The $(C_P^E)_{123}$ data were next analyzed in terms of Graph and Flory's theories.

Graph theory

Excess heat capacities of ternary mixtures

The analysis of excess molar volumes, V^E, excess isentropic compressibilities, κ_S^E, excess molar enthalpies, H^E, and excess heat capacities, C_P^E, and IR studies of [emim][BF_4] (1) + 2-Py or NMP or cyclopentanone or cyclohexanone (2); 2-Py or NMP (1) + cyclopentanone or cyclohexanone (2) mixtures [37–39, 63] have shown that (1) [emim][BF_4] exists as monomer; (2) 2-Py or NMP

exists as associated molecular entities; and (3) cyclopentanone or cyclohexanone is characterized by dipole–dipole interactions. The [emim][BF_4] (1) + 2-Py or NMP (2) + cyclopentanone or cyclohexanone (3) mixtures can, therefore, be assumed to involve processes; (a) establishment of unlike (i) $1-2_n$ ($n=2$), (ii) 2_n-3_n ($n=2$) and (iii) $1-3_n$ ($n=2$) contacts; (b) unlike contact formation between the constituent molecules ruptures self-association or dipole–dipole interactions with (i) 2_n and (ii) 3_n molecules to form 2 and 3 molecules and enhances the randomness in mixed state; (c) 1, 2 and 3 constituent molecules undergo interactions to form (i) 1:2, (ii) 2:3 and (iii) 1:3 molecular complexes, which in turn leads to non-randomness in mixed state as compared to pure state. If χ_{12}, χ_{23}, χ_{13}; χ_{22}, χ_{33} and $\chi'_{12}, \chi''_{12}, \chi'''_{12}$ are molar interaction energy parameters for $1-2_n$, 2_n-3_n, $1-3_n$ unlike contacts, respectively, rupture of associated molecular entities 2_n and 3_n, and molecular interactions between 1, 2 and 3 constituent molecules to yield randomness and non-randomness, respectively, in mixed state, then change in thermodynamic property, (ΔC_P), due to processes (a) (i–iii), (b) (i–ii) and (c) (i–iii) were given [56, 64–69] by relation:

$$\begin{aligned}\left(C_P^E\right)_{123} &= \left[\frac{x_1x_2v_2}{\sum_{i=1}^{2}x_1v_1}\right]\left[\chi_{12}+x_1\chi_{22}+x_2\chi'_{12}\right]\\ &+\left[\frac{x_2x_3v_3}{\sum_{j=2}^{3}x_2v_2}\right]\left[\chi_{23}+x_3\chi''_{12}\right]\\ &+\left[\frac{x_3x_1v_3}{\sum_{k=3}^{1}x_2v_2}\right]\left[\chi_{13}+x_3\chi_{33}+x_1\chi'''_{12}\right]\end{aligned} \tag{4}$$

As $v_2/v_1 = {}^3\xi_1/{}^3\xi_2$, where $({}^3\xi_i)$, $({}^3\xi_i)_m$ ($i=1$ or 2 or 3), etc., are connectivity parameters of third degree of molecules in pure as well as mixed state and are defined [70] by

$${}^3\xi = \sum_{m<n<o<p}\left(\delta_m^v\delta_n^v\delta_o^v\delta_p^v\right)^{-0.5} \tag{5}$$

The δ_m^v, etc., values reflect the valency of the atoms forming the bond and are expressed as [71] $\delta^v = Z_m - h$, where Z_m is the maximum valency of the atom and h is the number of hydrogen atom attached to it. The ${}^3\xi$ values for the constituent molecules were taken from literature [37, 61, 63] consequently; Eq. 4 was reduced to

$$\begin{aligned}\left(C_P^E\right)_{123} &= \left[\frac{x_1x_2({}^3\xi_1/\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right]\left[\chi_{12}+x_1\chi_{22}+x_1\chi'_{12}\right]\\ &+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right]\left[\chi_{23}+x_3\chi''_{12}\right]\\ &+\left[\frac{x_3x_1({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right]\left[\chi_{13}+x_3\chi_{33}+\chi'''_{12}\right]\end{aligned} \tag{6}$$

For the present mixtures, we assumed that $\chi_{12} \cong \chi'_{12} = \chi^*_{12}$; $\chi_{23} \cong \chi''_{12} = \chi^*_{23}$; $\chi_{13} \cong \chi'''_{12} = \chi^*_{13}$ and $\chi_{22} \cong \chi_{33} = \chi^*$ and then Eq. 6 was reduced to

$$\begin{aligned}\left(C_P^E\right)_{123} &= \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right]\left[(1+x_2)\chi^*_{12}+x_1\chi^*\right]\\ &+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right]\left[(1+x_3)\chi^*_{23}\right]\\ &+\left[\frac{x_3x_1({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right]\left[(1+x_1)\chi^*_{13}+x_3\chi^*\right]\end{aligned} \tag{7}$$

Equation 7 contains four unknown χ^*_{12}, χ^*_{23}, χ^*_{13} and χ^* parameters. These parameters were commuted utilizing $\left(C_P^E\right)_{123}$ data at four arbitrary compositions and then subsequently used to predict $\left(C_P^E\right)_{123}$ data at other values of x_1 and x_2. Such $\left(C_P^E\right)_{123}$ values are listed in Table 3 and also compared with their corresponding experimental values. The χ^*_{12}, χ^*_{23}, χ^*_{13} and χ^* parameters and mean deviations between $\left(C_P^E\right)_{123}$ values and $\left(C_P^E\right)_{123}$ values calculated by Graph theory, $\sigma\left(C_P^E\right)_{123\,\mathrm{Graph}}$, are also reported in supporting Table 2S. Perusal of data in Table 3 indicates that $\left(C_P^E\right)_{123}$ values determined by Graph theory are in agreement with experimental data which in turn support various assumptions in deriving Eq. 7.

Flory's theory

Differentiating Flory's expression for excess molar enthalpies [72, 73] for binary and ternary mixtures with respect to the temperature, T, and excess heat capacities, $\left(C_P^E\right)_{123}$, for ternary mixtures was expressed by

$$\left(C_P^E\right)_{123} = -\sum_{i=1}^{3}\frac{x_iP_i^*\tilde{v}_i^*\alpha_i}{\tilde{v}_i} + \left(\frac{\alpha}{\tilde{v}}\right)\left[\sum_{i=1}^{3}x_iP_i^*v_i^* - \sum_{i=1}^{3}x_iv_i^*\theta_j\chi^{**}_{12}\right] \tag{8}$$

where $\tilde{v}_i^*$,P_i^* and $\tilde{v}_i$($i=1$ or 2 or 3) are the characteristic volume, characteristic pressure and reduced volume of pure component (i) and $\tilde{v}$ is reduced volume of mixture and all the terms have the same significance as described elsewhere [72, 73]. The Flory parameters for the liquids under investigations are taken from literature [61, 63]. Flory assumed that interaction energy parameters, χ^{**}_{12}, etc., for sub-binaries of (1 + 2 + 3) ternary mixtures, which in turn are evaluated by using their H^E data at equimolar composition, were assumed to be independent of temperature by Flory. However, Benson and D' Arcy [74] assumed that χ^{**}_{12}, etc., parameters for binary mixtures should be a function of temperature. Consequently,

$(C_P^E)_{123}$ values for ternary mixtures were then expressed by relation

$$(C_P^E)_{123} = -\sum_{i=1}^{3}\frac{x_i P_i^* \tilde{v}_i^* \alpha_i}{\tilde{v}_i} + \left(\frac{\alpha}{\tilde{v}}\right)\left[\sum_{i=1}^{3} x_i P_i^* v_i^* - \sum_{i=1}^{3} x_i v_i^* \theta_j \chi_{12}^{**}\right] + \sum_{i=1}^{3}\frac{x_i v_i^* \theta_j}{\tilde{v}}\left(\frac{\partial \chi_{12}^{**}}{\partial T}\right) \quad (9)$$

The reduced volumes, $\tilde{v}$, and thermal coefficient, α, of ternary mixtures were calculated using

$$\tilde{v} = \left(V_{123}^E + \sum_{i=1}^{3} x_i v_i\right) \Big/ \sum_{i=1}^{3} x_i v_i^* \quad (10)$$

$$\alpha = \sum_{i=1}^{3} x_i \alpha_i \quad (11)$$

where V_{123}^E represent excess molar volumes of ternary (1 + 2 + 3) mixtures. Such χ_{12}^{**}, etc., values for the various binaries were calculated using H^E value at equimolar composition that was taken from literature [37, 61, 63]. The calculated $(C_P^E)_{123}$ values via Eqs. 8–11 for the present mixtures are compared with experimental values and presented in Table 3. The values of χ_{12}^{**}, etc., are recorded in supporting Table 2S. Examination of data in Table 3 indicates that Flory's theory correctly predicts the sign of $(C_P^E)_{123}$ values. However, quantitative agreement is poor. The failure of theory to correctly predict the sign of $(C_P^E)_{123}$ may be due to strong interactions between unlike molecules.

Conclusions

The excess heat capacity, $(C_P^E)_{123}$, values of the 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + pyrrolidin-2-one or 1-methylpyrrolidin-2-one (2) + cyclopentanone or cyclohexanone (3) mixtures have been evaluated by using their molar heat capacities, C_P. The $(C_P^E)_{123}$ of the studied ternary mixtures are positive over entire mole fraction of (1) and (2) which in turn suggest that capability of cyclohexanone or cyclopentanone molecules to build a non-random structure in mixed state is superior to the effect caused by disruption of associated NMP or 2-Py entities, and interactions between [emim][BF_4]:NMP or 2-Py molecular entities. While $\left(\frac{\partial C_P^E}{\partial T}\right)$ for [emim][BF_4] (1) + 2-Py (2) + cyclopentanone or cyclohexanone (3) mixtures are positive, those for [emim][BF_4] (1) + NMP (2) + cyclopentanone or cyclohexanone (3) mixtures are negative. The $(C_P^E)_{123}$ data have been analyzed in terms of Graph and Flory theories. It has been observed that $(C_P^E)_{123}$ values obtained from Graph theory compare reasonably well with the experimental values.

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